# TANNING WITH TRIS(HYDROXYMETHYL)NITROMETHANE AND RESORCINOL

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## ABSTRACT

Tris(hydroxymethyl)nitromethane† (THNM) reacts with resorcinol under mildly alkaline conditions to yield tanning agents. These can be formed in the presence of skins to give an *in situ* tannage. A procedure and the resulting leathers are described.

The presence of a nitro group in THNM activates the methylol groups by electron withdrawal. This permits their reaction with resorcinol and amino groups in collagen under mild conditions to produce leather by the Mannich reaction. This reactivity is in contrast to the inertness of tetrakis(hydroxymethyl)methane under the same conditions.

## INTRODUCTION

Resorcinol and formaldehyde have been shown to react under both strongly acid (1) and mildly alkaline (2) conditions to produce tanning agents in the presence of hides and skins which yield leather that dries out soft after wetting and has a high hydrothermal stability.

Resorcinol also reacts with tetrakis(hydroxymethyl)phosphonium chloride in alkaline solution in an *in situ* tannage to yield commercial quality leather (3–5). The tannage is perspiration-resistant and has the interesting ability to eliminate after-glow on chrome-tanned leather (5–7).

The commercial availability of an acrolein-formaldehyde polymer led to an investigation of its reaction with resorcinol, using the same procedure. Good quality sheepskin lining and work-glove leathers were produced (8, 9).

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†Indexed by *Chemical Abstracts* as 2-(hydroxymethyl)-2-nitro-1,3-propanediol.

Tetrakis(hydroxymethyl)methane, commonly known as pentaerythritol, had no tanning action when tested alone or in combination with resorcinol in acidic or alkaline solutions. The methylol groups are not sufficiently reactive to combine with resorcinol and the ε-amino group of the lysinyl residue of collagen through a Mannich reaction in dilute aqueous solution at room temperature.

Presumably, if the hydroxymethyl groups could be activated sufficiently, they would react in the desired manner. They can be activated substantially by introducing a group that withdraws electrons strongly, such as a nitro- or a cyano-group. The availability of tris(hydroxymethyl)nitromethane (THNM) prompted an investigation of the tanning action of a mixture of this compound and resorcinol. The results are of scientific interest.

## EXPERIMENTAL

After preliminary tests, the following procedure was used to tan six cabretta skins and six domestic sheepskins in separate runs of three skins each. The percent of chemicals is based on the drained pickled weight of the skins, except for sodium sulfate, which is based on the solution.

| | |
|---|---|
| Pickled degreased cabretta sheepskins | 100 % |
| Water | 200 % |
| Sodium sulfate, anhydrous (solution basis) | 10 % |
| Sodium acetate | 3 % |
| Resorcinol | 7.2% |
| Tris(hydroxymethyl)nitromethane | 10.0% |
| Run ½ hour; pH 4.7; temperature 35°C. | |
| Sodium carbonate, anhydrous | 2.0% |
| Run 1 hour; pH 6.7; temperature 30°C. | |
| Sodium carbonate, anhydrous | 1.0% |
| Run 1 hour; pH 8.3; temperature 26.5°C. | |
| Run 2 hours; pH 8.3; temperature 26°C. | |
| Run 3 hours; pH 8.3; temperature 24°C.; $T_s$ 91°C. | |
| Wash 20 minutes and drain overnight. | |
| Sulfuric acid | 1.8% |
| Water | 200 % |
| Run 1 hour; pH of skin approximately 3.6; $T_s$ 87°C. | |
| Wash and treat with BSM-11.‡ | |

The sodium sulfate, sodium acetate, resorcinol and THNM were added at one time to the water in a small, warm drum and the skins were entered after the chemicals were dissolved. It was also found that the sodium carbonate solu-

‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

tion could be added in one feed after 1.5 hours of drumming with no adverse effect. Tanning action is slow below pH 8.0. The liquor is colorless to light yellow initially and darkens to an orange-brown after it is made alkaline. A 1:1 molar ratio of THNM and resorcinol was found to be satisfactory. After a seven-hour tannage, there was usually a positive test for resorcinol. The cabretta sheepskins had a shrink temperature of 90–91°C. After a 24-hour tannage, there often continued to be a positive test for resorcinol and the shrink temperature of the skins was about the same, 90–93°C. The skins were also darker in color and fuller. The color was lightened considerably by the acidification, and the shrink temperature dropped a few degrees.

The cabretta skins were processed into finished garment or glove leather at a tannery. The domestic sheepskins were processed into shoe-lining leather and inexpensive dress-glove leather at another tannery. The methods of the ASTM-ALCA were used for testing the leathers (10). The Tentative Method for Measuring Resistance of Chrome-Tanned White Shoe Upper Leather to Artificial Perspiration (11) was used with a modified artificial perspiration solution. Twenty grams of urea per liter of solution was used instead of 1.67 grams, given in the method (12).

Samples of THNM-resorcinol-tanned Iranian sheepskins were retanned separately with basic chromium sulfate, a blend of vegetable tannins, or glutaraldehyde, using conventional procedures.

## RESULTS AND DISCUSSION

### Properties of the Leather

The cabretta leather was round and mellow but was too tight for glove leather, as might be expected from an organic tannage. The color of the leather was light brown or tan and could be mistaken for that of a vegetable tannage.

The lining leather made from the domestic sheepskins had good appearance, temper and tensile strength. It was satisfactory commercial leather. Those skins processed into inexpensive dress-glove leather were too firm and tight for this use, but were otherwise satisfactory. The tensile strength was adequate. The data on the physical tests of some of these leathers appear in Table I.

TABLE I

PHYSICAL DATA ON FINISHED LEATHER

| Test | Cabretta Glove | Domestic Sheep Lining |
|---|---|---|
| Tensile strength, PSI | 5625 | 3440 |
| Slit tear, perpendicular, lbs. | 13 | 14 |
| Ball burst, lbs./in. thickness | 3955 | 2920 |

All leathers were resistant to the accelerated perspiration test, as can be seen in Figure 1.

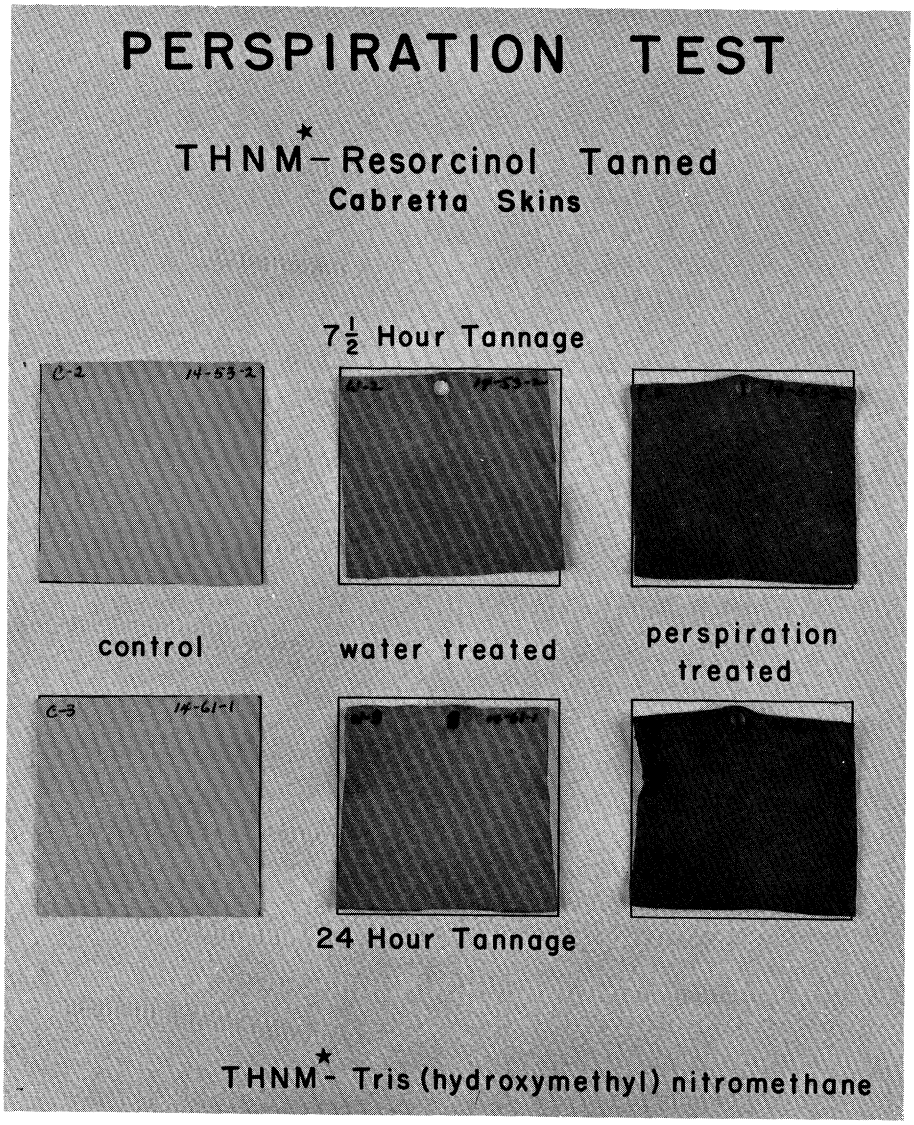
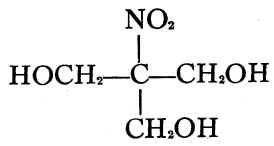



FIGURE 1.—Perspiration test on tris(hydroxymethyl)nitromethane-resorcinol tanned cabretta skins.

## Characteristics of the Tannage

Tris(hydroxymethyl)nitromethane, also known as 2-(hydroxymethyl)-2-nitro-1,3-propanediol, has the following formula:



It is prepared from trioxymethylene and nitromethane. It is reported to release formaldehyde slowly in alkaline solution. It was therefore necessary to establish that the tanning was not due to formaldehyde or its reaction products with resorcinol. THNM alone yielded a $T_s$ of 65° or 70°C. on sheepskins after eight days at a pH of 8.0 or 9.0, respectively. The resulting samples could not be characterized as leather (Table II). The addition of resorcinol to the sample at a pH of 8.0 raised the $T_s$ to 86°C. in 24 hours and produced "leathering." Large amounts of THNM alone, 20 and 40 percent on the pickled weight of the

TABLE II

DATA ON ATTEMPTED TANNAGE WITH TEN PERCENT THNM

| Final pH | Time (Hrs.) | $T_s$* (°C.) | Product |
|---|---|---|---|
| 1.7 | 192 | 43 | Untanned raw skin |
| 4.6 | 192 | 56 | " " " |
| 8.4 | 192 | 65 | " " " |
| 8.8 | 192 | 70 | Poor; thin, firm |

*$T_s$ of the fat-liquored, dried leather.

skin, gave similar results. After 20 days at pH 8.0, the shrinkage temperatures of the skin were 62 and 56°C., respectively. Again the samples did not have the characteristics of leather. Resorcinol was added, and after 24 hours the $T_s$ was raised to 89°C. The samples were tanned and had leather characteristics. The very dark brown color on the alkaline side is characteristic of nitro compounds and was much darker than that obtained with resorcinol and formaldehyde at the same pH. The $T_s$ was also lower.

A large number of tests were run on 50-gram pieces of pickled Iranian hair sheep to determine the most desirable molar ratios and quantities of the reactants. It was found that a 1:1 ratio was as effective as a higher ratio of THNM to resorcinol. This is in contrast to the results obtained when using formaldehyde with resorcinol, in which a ratio of three moles of the aldehyde to one of the phenol produced the best results (1). This fact may be related to the presence of three methylol groups in one molecule of THNM, although it would be expected that steric hindrance would reduce the availability for reaction of the second, and especially the third, methylol group in a single molecule.

Ten percent of THNM and 7.2 percent of resorcinol were selected as entirely adequate amounts of chemicals to yield well-tanned leather, although half of these amounts also produced mellow, full leather and might be adequate for many purposes. The shrink temperature was quite uniform at 86°C. in a 24-hour tannage over a wide range of amounts, but this is only one property of leather.

## TABLE III

### COMPARISON OF SHRINKAGE TEMPERATURE AND LEATHER WITH CHANGES IN pH (10 PERCENT THNM AND 7.2 PERCENT RESORCINOL)

| Final pH | Tannage (Hrs.) | $T_s$* (°C.) | Leather |
|---|---|---|---|
| 1.7 | 48 | 56 | Untanned |
| 3.5 | 216 | 55 | " |
| 4.7 | 48 | 58 | " |
| 6.7 | 48 | 79 | Poor to fair |
| 7.3 | 28 | 78 | Fair |
| 8.0 | 28 | 88 | Good |
| 9.0 | 24 | 99 | Good |

*$T_s$ of the fat-liquored, dried leather.

The *in situ* tannage took place only under neutral to mildly alkaline conditions (Table III). Essentially no tanning occurred below a pH of 5.0. A pH of 8.0 was preferable. While the tanning was somewhat more rapid and the $T_s$ was higher at pH 9.0, the leather was much darker. From a practical standpoint, it is not desirable to tan on the alkaline side, since this is not a conventional procedure and the fibers appear to be separated to such an extent that the leather is too fluffy and is referred to as "punky" or "mushy." It is well known that sodium sulfate is preferable to sodium chloride to minimize alkaline swelling, but it is not eliminated. While the leather made in this work was satisfactory, tests were not extensive enough to evaluate this property thoroughly.

Various combination tannages were carried out to confirm that retanning would be normal and straightforward, which was the case. In one instance glutaraldehyde was added to the THNM-resorcinol liquor at the beginning. The $T_s$ was raised some 5°C. by this dialdehyde. A four percent chrome retannage raised the $T_s$ from 86°C. to 100°C., and a blend of vegetable extracts raised the $T_s$ 7–8°C.

It is assumed that the tanning mechanism is a Mannich reaction, as postulated in previous publications (1, 5, 8). Resorcinol provides the active hydrogen atoms, collagen the amine groups, and THNM the equivalent of an aldehyde function by its methylol groups.

## SUMMARY

The use of resorcinol in an *in situ* tannage has been extended to its combination with tris(hydroxymethyl)nitromethane. The methylol groups in the latter compound have been activated by electron withdrawal by the nitro group so that they will react with resorcinol in dilute aqueous solution at room temperature to form tanning compounds. Leather of acceptable quality has been made from sheepskins.

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